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Growth and characterization of a new metal - organic nonlinear optical thiourea potassium magnesium sulphate single crystals

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ABSTRACT

A new semiorganic nonlinear optical thiourea potassium magnesium sulphate (TPMS) crystal was synthesized. TPMS single crystals were grown from aqueous solution by slow evaporation technique. The solubility of TPMS was determined for various temperatures. Single crystal X-ray diffraction (XRD) study was carried out to identify the lattice parameters. Various diffracting planes of the grown crystal were identified from the powder X-ray diffraction study. Fourier transform infrared (FT-IR) studies confirm the various functional groups present in the grown crystal. The transmission spectrum of this crystal shows that the lower cut off wavelength lies at 224 nm. The thermal analysis confirmed that the crystal is stable up to 223°C. Microhardness studies revealed that the hardness of the grown crystal increases with an increase in load. The nonlinear optical (NLO) property of the grown crystal has been confirmed by Kurtz powder second harmonic generation (SHG) test.

Keywords : NLO, XRD, FT-IR, DTA/TGA, Micro hardness.

INTRODUCTION

Efficient nonlinear optical (NLO) crystals are required for laser devices due to technological importance in the fields of opto electronics, signal processing, instrumentation and optical communication [1, 2]. In the recent years semi organic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, high damage threshold and high mechanical strength than organic NLO crystals. In semi organic materials the organic ligand is ionically bonded with inorganic host and hence semi organic crystals are having higher chemical stability and mechanical strength [3]. Among the semi organic NLO materials, metal complexes of thiourea, have a low UV cut off wavelength which is applicable for frequency conversion and second harmonic generation [4-8]. Thiourea is a centrosymmetric molecule, when coordinated with metal ions it becomes non-centrosymmetric material to exhibit nonlinear optical activity. Zinc thiourea sulphate (ZTS) is an excellent NLO material for type II second harmonic generation and is nearly 1.2 times more nonlinear than KDP [9].

Some of the efficient NLO crystals of metal organic complexes of thiourea such as zinc thiourea chloride (ZTC) [10], bisthiourea cadmium chloride (BTCC) [11] and tristhiourea magnesium sulphate (MTS) [12] have already been reported. The theory of double- radical model (organic conjugated molecular groups are included in the distorted polyhedron of coordination complex) was brought up in 1987 [13]. With the guidance of this theory, many metal- organic coordination complexes of thiourea materials, with good NLO effect have been designed and

synthesized [14- 20]. In this present investigation, a new metal- organic NLO crystal crystal of thiourea potassium magnesium sulphate (TPMS) is reported for the first time and the grown crystals have been characterized by various characterization studies.

MATERIALS AND METHODS

2.1 Synthesis

TPMS salt was synthesized by dissolving thiourea (AR grade), potassium sulphate (AR grade) and magnesium sulphate hepta hydrate (AR grade) in the ratio 3: 0.25: 0.75 in double distilled water. The prepared solution was slightly heated up and solvent was allowed to evaporate. TPMS was synthesized as per the following reaction.

$3[CS(NH_2)_2] + K_2SO_4 + MgSO_4.7H_2O \rightarrow K_2Mg[CS(NH_2)_2]_3SO_4.7H_2O$

The synthesized TPMS salt was purified by successive recrystallization processes.

2.2 Crystal growth

In order to grow bulk single crystals of TPMS, the solubility of the synthesized material was determined at different temperatures (35- 45°C). The gravimetric method was adopted to determine solubility and this was carried out in a constant temperature bath (±0.01°C). The solution was stirred continuously for 6 hours in a magnetic stirrer. Fig. 1 shows that TPMS has a positive solubility- temperature gradient. The saturated solution prepared at 35°C was filtered using Whatman filter paper. The filtered solution was taken in the beaker and closed with perforated cover and was kept in a constant temperature bath maintained at 35°C. The solvent was allowed to evaporate slowly. TPMS crystal of size 20x 25x 10 mm^3 was harvested from the mother solution with a time span of 30 days. The grown TPMS crystal is shown in Fig. 2.

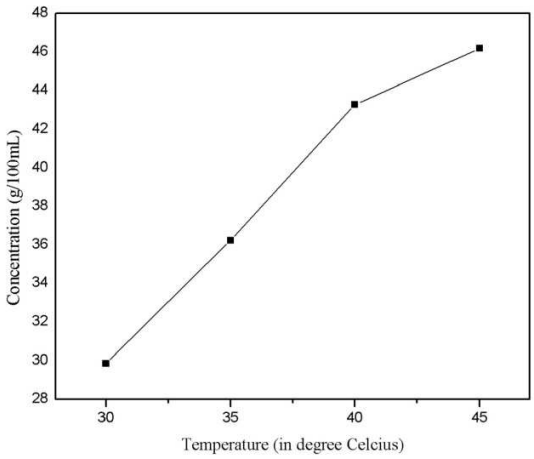

Fig. 1: Solubility curve of TPMS

Fig. 2: As grown crystal of TPMS

RESULTS AND DISCUSSION

3.1 X- ray diffraction analysis.

The grown crystals were subjected to single crystal X- ray diffraction using an ENRAF NONIUS CAD-4 diffractometer with Mo Kα (λ= 0.71073Å) radiation at room temperature. The crystal belongs to orthorhombic system. The observed unit cell parameters are given in Table 1 and the observed values are compared with tristhiourea magnesium sulphate [12].

Table 1 :Comparison of lattice parameters of TPMS with MTS

parameters	TPMS Present work	MTS [12]
a(Å)	7.79	5.482
b(Å)	11.17	7.672
c(Å)	15.50	8.562
Cell Volume(Å)^3	1349	360

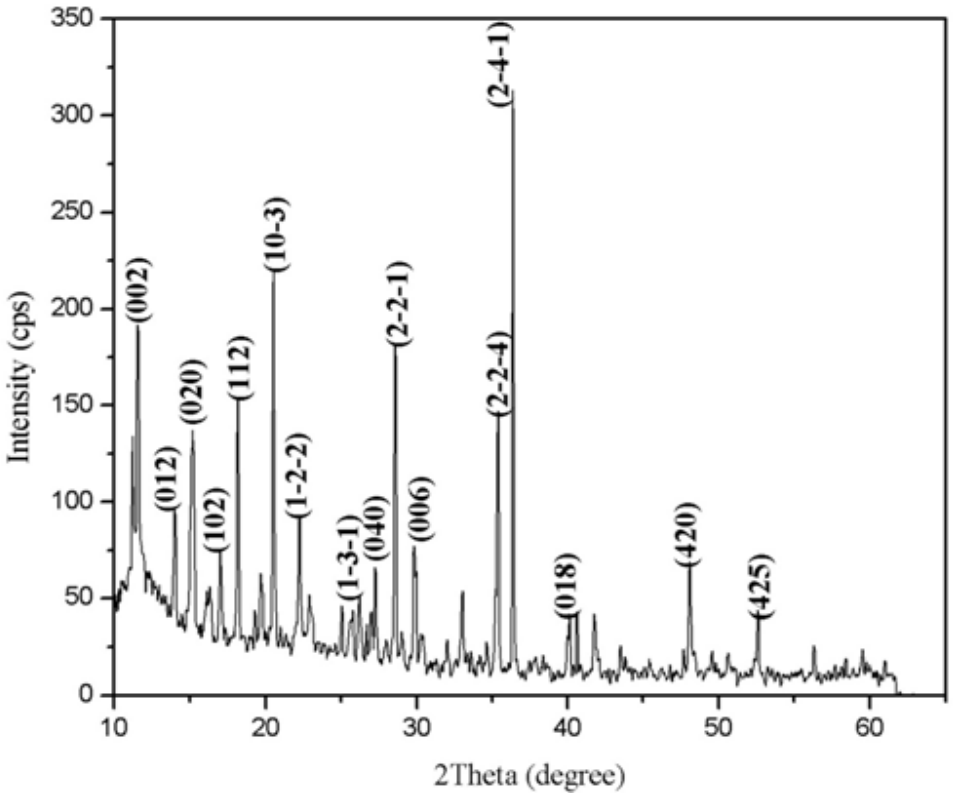

Fig. 3: Indexed powder XRD pattern of TPMS

Powder XRD pattern of TPMS was recorded using a Rich Seifert diffractometer with Cu Kα (λ= 1.54059 Å) radiation. The powder sample was scanned over the range 10- 80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (Fig. 3).

3.2 FT-IR analysis

Fourier transform infrared (FT-IR) spectrum was recorded with a Perkin- Elemer RXI spectrometer using KBr pellet technique in the wavenumber range 400- 4000 cm^{-1} in order to confirm the presence of functional groups and the coordination of ligand- to- metal ions. The recorded FT-IR spectrum of the TPMS compound is shown in Fig. 4. In the high frequency region sharp intense peaks observed at 3310 and 3192 cm^{-1} are attributed to asymmetric and symmetric stretching vibrational modes of NH_2 of thiourea molecule [21]. The NH stretching of thiourea is observed to form a broad envelope between 3300 and 1600 cm^{-1} due to its hydrogen bonding interaction with the neighbouring anion complex. The C= S stretch of thiourea is slightly shifted to lower value than pure thiourea [22] due to its coordinate interaction with metal ions (Table 2). Besides, this interaction is also evident be a shift in the N- C- N stretch of thiourea to higher value in TPMS crystals compared to pure thiourea [23]. The C= S coordination to metal ion enhances the resonance delocalization of NH_2 lone pair electrons, thus providing more double bond character for N- C- N, and hence both symmetric and asymmetric N- C- N stretching is shifted to higher values [24].

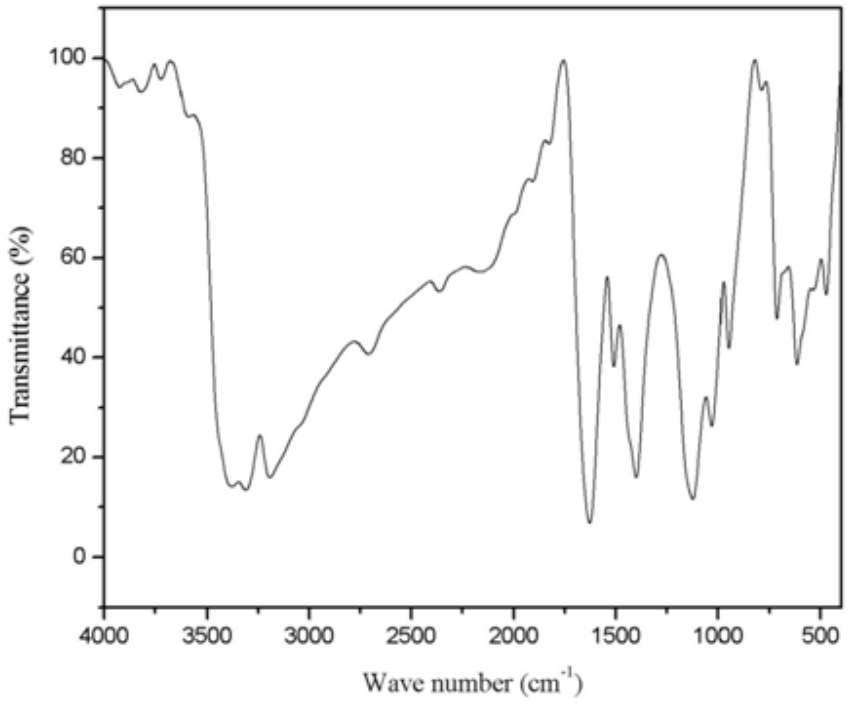

Fig. 4: FT-IR spectrum of TPMS

In pure thiourea, C= S is bonded to NH_2, whereas in TPMS crystals it is bonded to metal ions and therefore the C= S stretching vibration is also shifted to lower values from 730 to 713 cm^{-1} and this shifting of C= S stretching frequency confirms the coordination of metal- sulphur bond [25]. The intense band at 615 cm^{-1} is due to NH_2 bending vibration. The peak at 1627 cm^{-1} with very strong intensity could be assigned to NH_2 asymmetric bending vibrations [26]. The strong band centered at 1122 cm^{-1} corresponds to NH_2 rocking vibrations. The N- C- N symmetric stretching vibration of pure thiourea [23] occur at 1470 cm^{-1} and in TPMS this frequency is slightly increased and observed at 1508 cm^{-1} because of the greater double bond character of C- N bond. The strong peak at 1399 cm^{-1} can be assigned to C= S asymmetric stretching vibration of TPMS complex. From the FT-IR spectral analysis, the presence of functional groups and the coordination ligands of TPMS were confirmed and the assignment of functional groups is compared with pure thiourea, zinc thiourea sulphate (ZTS) [27] and tristhiourea magnesium sulphate (MTS) [12] and is given in Table 2.

Table 2 :Comparison of IR bands of TPMS with thiourea, ZTS and MTS

Thiourea [23] cm^{-1}	ZTS [27] cm^{-1}	MTS [12] cm^{-1}	TPMS Present work cm^{-1}	Assignments
3376	3378	3368	3310	$\upsilon_{as}(NH_2)$
-	3306	3298	-	$\upsilon_{as}(NH_2)$
3167	3206	-	3192	$\upsilon_{s}(NH_2)$
1627	1633	1611	1627	$\delta_{as}(NH_2)$
-	1515	1472	1508	υ_{s}(N-C-N)
1417	1404	1413	1399	υ_{as}(C=S)
1089	1126	1084	1122	$\rho(NH_2)$
740	717	730	713	υ_{s}(C=S)
-	-	-	615	$\delta(NH_2)$
411	424	431	427	δ_{s}(N-C-N)

υ_{as}-asymmetric stretching, υ_{s}-symmetric stretching, δ_{as}-asymmetric bending, ρ- rocking, δ-bending, δ_{s}- symmetric bending

3.3 UV- vis studies

UV- vis transmittance spectrum of TPMS crystal of thickness 2 mm was recorded using Perkin Elmer- lambda 35 UV- vis spectrophotometer in the range of 190- 1100 nm and is shown in Fig. 5. The UV transparency lower cutoff

wavelength occurs at 224 nm. The absence of absorption of light in the visible region (330- 800 nm) enables the suitability of TPMS crystal for optoelectronic applications [28].

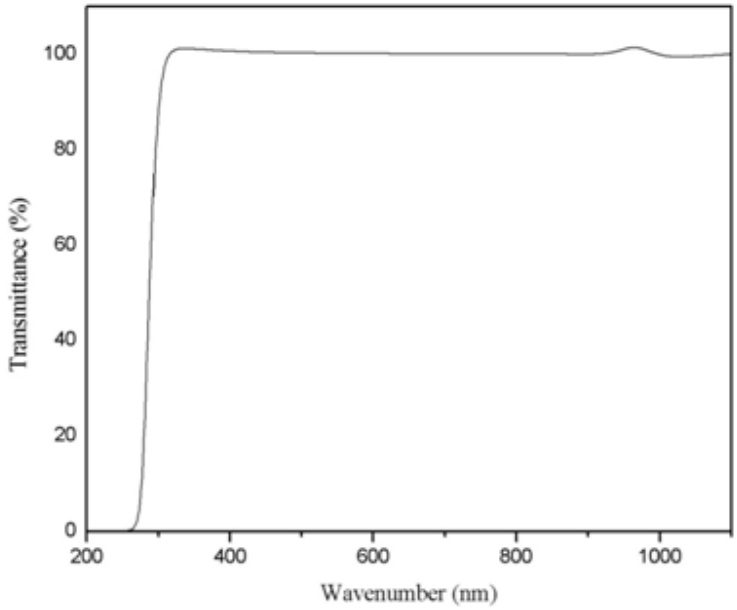

Fig. 5: Transmittance spectrum of TPMS crystal

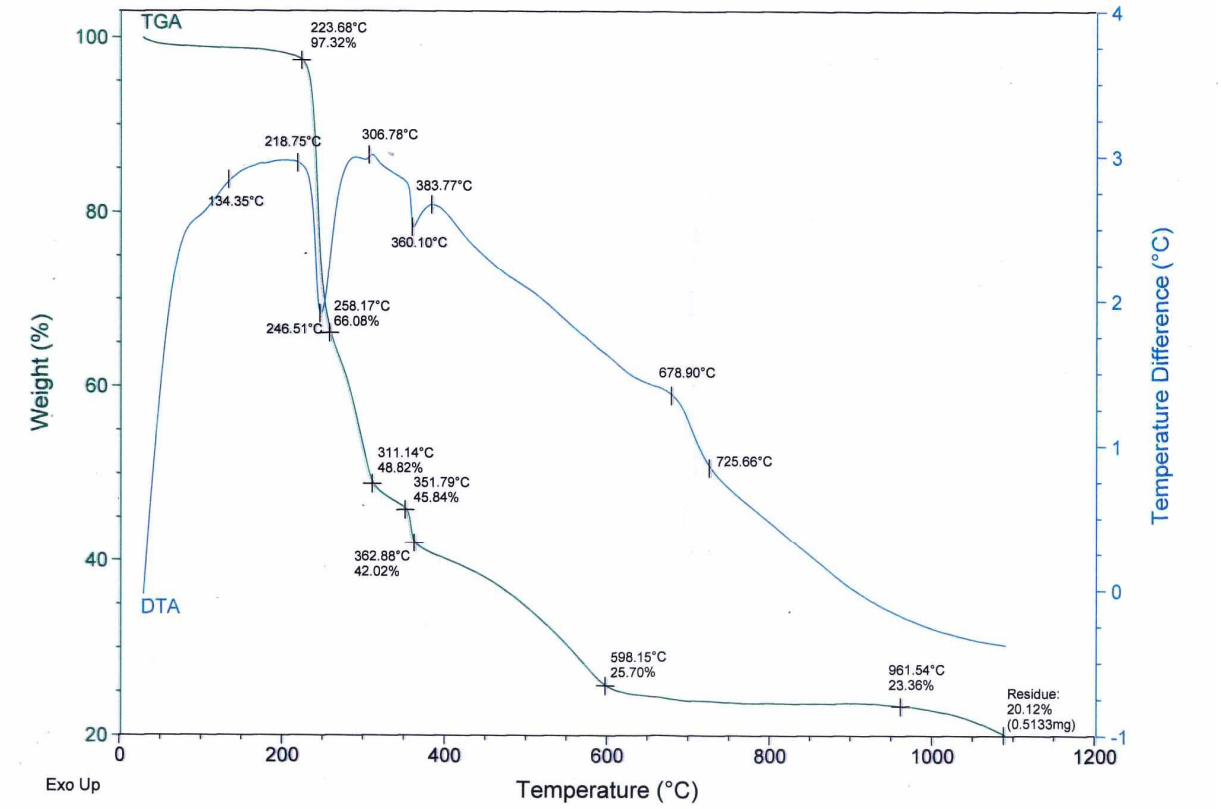

Fig.6: TGA/DTA curve of TPMS crystal

3.4 Thermal analysis

Thermal analysis was carried out using SDT Q600V 8.3 build 101 simultaneous DTA/TGA analyzer in the nitrogen atmosphere. The thermo gravimetric analysis(TGA) and differential thermal analysis (DTA) were carried out for a sample of weight 2.5510 mg in the temperature range 20- 1200°C at a heating rate of 20°C/min in nitrogen atmosphere (Fig. 6). From TGA it is observed that the crystal TPMS has good thermal stability up to 223.68°C as there is no weight loss below that temperature. The absence of weight loss around 100°C showed that the absence of water molecule in TPMS crystal during the crystallization process [20]. The TGA curve also shows that there was a weight loss of about 55.30% in the temperature range 223.68- 362.88°C due to the liberation of volatile substance in the compound.

The DTA curve shows the exothermic peak at 218.75°C, the melting point of the substance and it undergoes irreversible endothermic transition. The second exothermic peak at 306.78°C indicates the major decomposition of the material. The sharpness of the endothermic peak show good degree of crystallinity of the grown crystal TPMS. The heat capacity at constant pressure C_p of TPMS crystal was measured by differential scanning calorimetric (DSC) analysis in the temperature range 20- 1200°C at the heating rate for the system calibration. Powdered sample weight of 2.5510 mg was placed in a sealed alumina DSC pan. The curve of TPMS is shown in Fig. 7. The specific heat of TPMS crystal at 246. 32°C was found to be 347.6 J/g/°C.

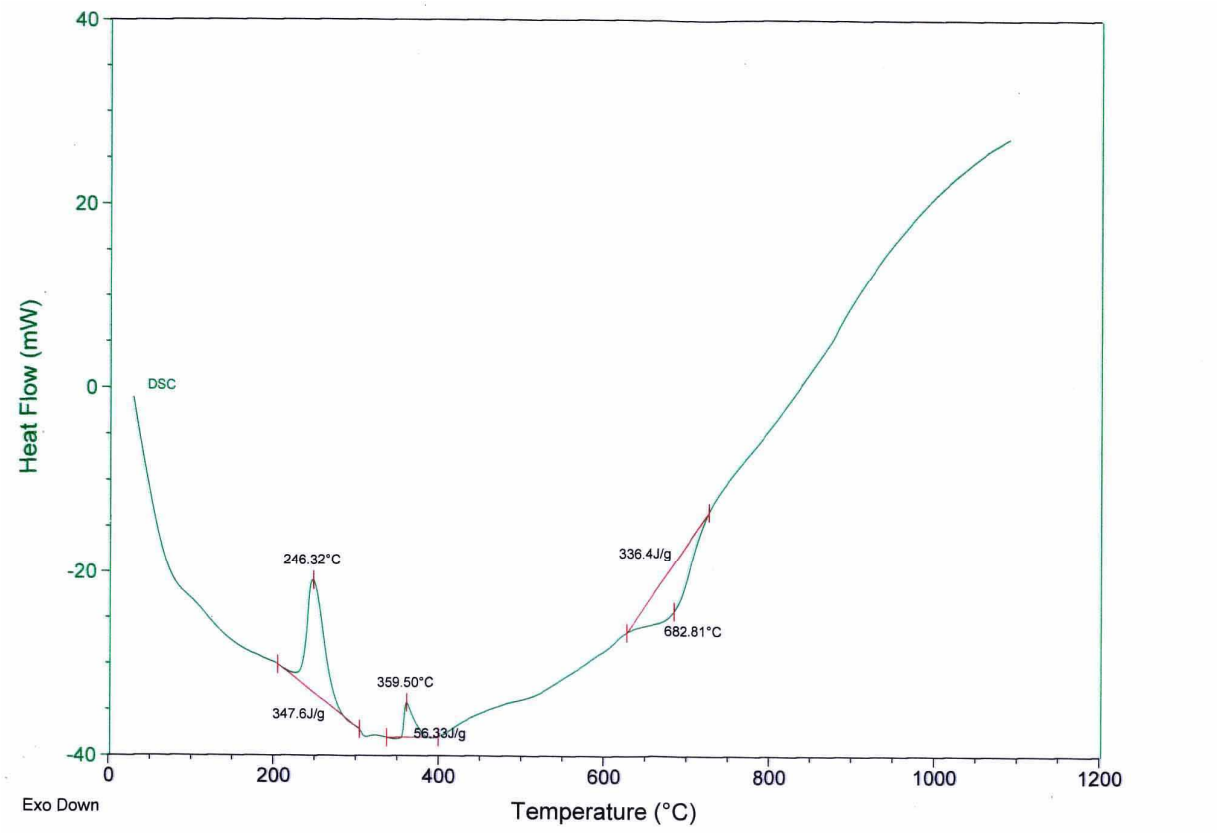

Fig. 7: DSC curve of TPMS

3.5 Microhardness studies

Microhardness test is one of the best methods for understanding the mechanical properties of materisls [29]. Hardness of the material is a measure of resistance that offers to deformation [30]. To find surface hardness of the grown TPMS crystal, microhardness was measured from 25 g to 100 g load using Shimadzu HMV- 2 microhardness tester. The transparent polished crystal free from cracks was selected for hardness measurement. Microhardness studies were carried out at room temperature and the time of indentation is kept constant at 5s for all the loads. The hardness of the material H_v was calculated by the relation, $H_v=1.8544\ P/d^2\ kg/mm^2$. Where P is the applied load and d is the mean diagonal length of the indentation. A graph was plotted for hardness versus P (Fig. 8) which shows

that the hardness increases with the increase of load. From Meyer's law P=and connecting the applied load (P) and diagonal length (d) of the indentation, work hardening coefficient 'n' was calculated. Here, 'a' is the constant for a given material. The work hardening coefficient was found to be 2.917 by taking a slope in the straight line of the graph drawn between log P and log d.

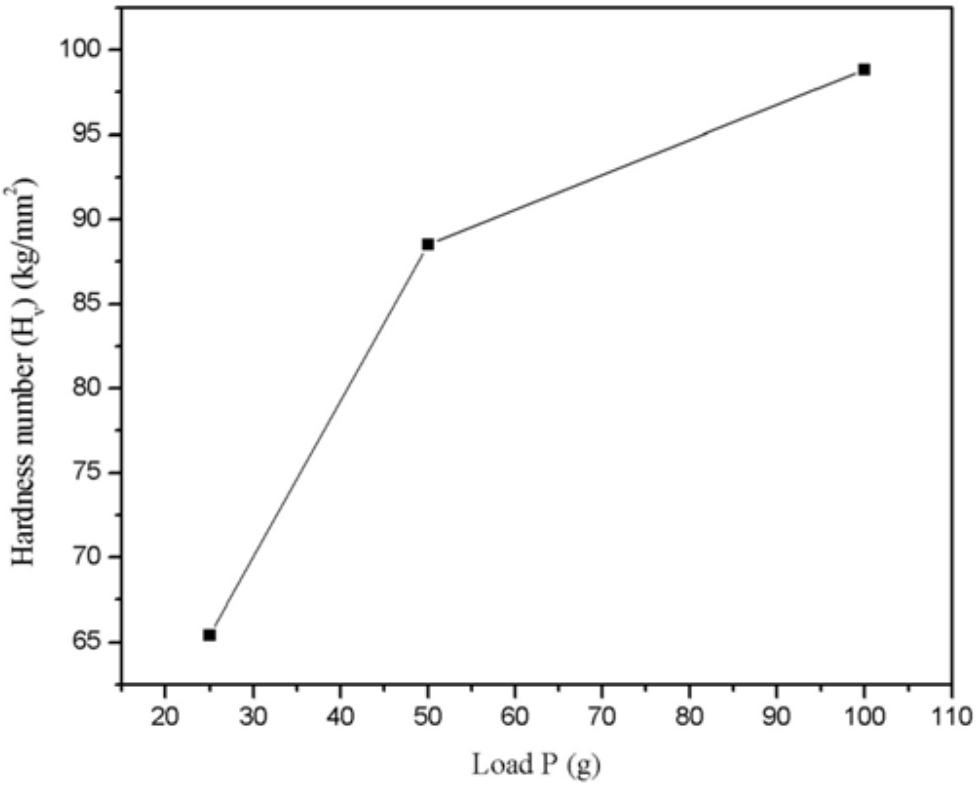

Fig.8: Variation of hardness versus P of TPMS

According to Onitsch [31] 'n' lies between 1 and 1.6 for hard materials and is greater that n 1.6 for soft materials [32, 33]. The 'n' value observed in the present studies is around 2.9 suggesting that the grown TPMs crystal is a relatively softer material. Yield strength can also be calculated using the relation [32] $б_y = (H_v/3)\ (0.1)^{n-1}$, where $б_y$ is the yield strength, H_v is the hardness of the material and n is the logarithmic exponent. According to the relation, the yield strength is found to be 2.660 MPa and hence the grown TPMS crystal has relatively low mechanical strength.

3.6 Nonlinear Optical studies

In order to confirm the NLO Property, the powdered sample of TPMS was subjected to a Kurtz and Perry [34] test. A high intensity Q- switched mode locked Nd: TAG laser of 1064 nm and a pulse width of 10 ns were passed through the powdered sample. The input laser beam was directed on the TPMS crystal powder to get maximum SHG. The emitted light passed through an IR filter was measured by means of a photomultiplier tube and oscilloscope assembly. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ=532 nm). The second harmonic signal of 59mV for TPMS was obtained for an input energy of 3.5 mJ/ pulse. The SHG efficiency of the TPMS crystal was evaluated by taking the microcrystalline powder of KDP as the reference material. The second harmonic signal for KDP is 65 mV. The powder SHG efficiency output was found to be 0.91 times greater with respect to KDP.

CONCLUSION

Good optical single crystal of thiourea potassium magnesium sulphate was grown from aqueous solution by the slow evaporation technique at room temperature. Unit cell parameters of the grown crystal TPMS were found by single crystal XRD analysis. Sharp peaks of powder XRD spectrum of the crystal show good crystalline nature of the compound. The presence of various functional groups was confirmed by FTIR analysis. From the TGA/DTA, the

crystal was thermally stable up to 223°C. The optical transmittance window and lower cut off wavelength of TPMS crystal were identified by UV- vis- NIR studies. The microhardness test shows that the hardness value increases with load, which confirms the reverse indentation size effects of the crystal. The SHG efficiency was found to be 0. 91 times that of KDP.

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